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STUDIES OF RESIDUES OF PARATHION AND PARAOXON IN CITRUS GROVES IN FRESNO AND TULARE COUNTIES, CALIFORNIA DURING THE SUMMER OF 1977

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SUMMARY

On July 16, 1977, a group of 39 men who were picking oranges in a grove near Terra Bella, California, became ill with symptoms that were diagnosed as organophosphate poisoning. The workers had been permitted to enter the grove to pick 22 days after application of ethyl parathion. The application rate was five pounds of pure parathion in 100 gallons of water per acre. Since this picking occurred eight days earlier than Department of Food and Agriculture regulations permit, charges of violation of worker safety reentry intervals were filed against those persons who were considered to have been responsible. Studies of the residues found raised questions as to whether the levels in this grove were typical for groves in the area that had been treated in a similar manner. Eighteen other groves, similarly treated in which no worker illnesses had been reported were studied. Residue levels in the soil and the total leaf extractions were similar to those in the orchard where the illnesses occurred. The leaf surface residue levels in the grove where the poisoning occurred were significantly higher than those in the other 18 fields studied at the time of worker entry and at 30 days after application when worker entry would have been legal.

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ORANGE PICKER POISONING INCIDENT

On July 16, 1977, a group of 39 men in a single orange picking crew became ill with what was diagnosed as organophosphate poisoning. The groves they had been picking in for two days prior to the onset of illness were studied and found to have negligible pesticide residues. All crew members became ill by the end of the first day of picking in the grove considered to have been the source of the poisoning. This grove had been treated 22 days earlier with 20 pounds of 25% wettable ethyl parathion powder in 100 gallons of water per acre for an actual application rate of five pounds of parathion per acre. It is not legal to allow workers to enter a grove so treated to pick until 30 days after application. Foliage and soil from this grove were sampled and significantly high residues of parathion and paraoxon were found on and in the leaves, on the surface of the fruit, and in the topsoil of the grove. The levels of residues found were considered sufficiently high to have been the source of poisoning. These high levels persisted in some areas of the grove beyond the expiration of the 30-day safety interval (see Tables 1, 2, 3, and 4).

STUDIES OF OTHER ORANGE GROVES OF THE AREA

It was decided to immediately study the residue levels of 18 other orange groves in the area. In a three-week period, orchards that had recently been treated with parathion, but using several different types of formulations, poundages per acre, amounts of water, types of spray equipment, and three different irrigation practices were sampled weekly. In addition, various methods of sampling were compared.

In these groves, parathion had been applied between nine and 47 days prior to the collection of the first samples. Applications were made with the following concentrations of parathion: three with 80% liquid concentrate, nine with 80% emulsifiable concentrate, five with 25% wettable powders, and one with 12.5% wettable powder. These pesticide formulations were diluted as little as in 100 to as much as 2,000 gallons of water per acre. This resulted in a range of one to 16 pounds of actual parathion applied per acre.

Soil and foliage samples were analyzed for parathion and paraoxon residues. Paraoxon has been established as 55 times more toxic dermally than parathion by Nabb et al and this value has been accepted by Gunther et al in toxicity evaluations of parathion residues. For this reason, data was converted to "parathion equivalents" as shown:

$$\text{Parathion residue in ppm} + \begin{pmatrix}\text{Paraoxon}\\ \text{residue}\\ \text{in ppm}\end{pmatrix} \times 55 = \text{Parathion equivalents in ppm}$$

This value more accurately reflects the worker safety hazard. Two foliage samples were gathered from each grove. One was analyzed for dislodgeable (surface) residue, and the other was analyzed for total residues (surface plus penetrated). The analytical methods used are given in the Appendix.

SAMPLING TECHNIQUES

During the study period, an additional analysis was made concerning the difference in sampling methods. Two foliage sampling methods were in common use at the time of the study. Most county inspection personnel remove the entire leaf from the tree at 50 different locations throughout the grove. The Department of Food and Agriculture personnel, as well as University research personnel in Calfiornia, usually collect leaf punches. By this latter method, a punch of two to three centimeters in diameter is taken from each of 80 leaves from approximately 20 trees along a diagonal across the grove.

In this study, six leaf punch samples were taken and three whole leaf samples were taken in a small section of a grove consisting of two rows of treated trees. Residues found are shown in Table 5. It can be seen that individual results by both methods vary widely. When averaged, however, they are not significantly different. Samples obtained by whole leaf sampling are more difficult to handle in the analytical laboratory, it is for this reason that leaf punching is preferred.

SURFACE RESIDUES ON LEAVES

Surface residues found were generally low. Thirteen groves sampled were found to have "parathion equivalents" of over 1 ppm (see Table 6). Seven of these same groves had residue levels over 5 ppm of parathion equivalents.

TOTAL RESIDUES IN LEAVES

Total residues (surface and penetrated) of parathion and paraoxon in the orange leaves were found to be highly variable and did not seem to be directly proportional to the amount of parathion applied.

Low and medium volume applications apparently resulted in generally higher residues than applications in which 1,000 or more gallons of water were used per acre. Rates of degradation varied widely.

After the expiration of the worker safety reentry interval of 30 days, the parathion equivalent residue ranged from 0.8 ppm to 195.9 ppm. Penetrated residue probably presents a minimal worker safety hazard since workers do not actually contact these residues.

SOIL RESIDUES UNDER TREES

Soil sampling was conducted by two methods. Method one involved the use of a plastic scraper to remove soil from the top millimeter of the surface from 40 locations in the grove with the samples collected just below the edge of the trees' outermost leaves and in an area not likely to have been irrigated. The soil was placed in a glass jar. Approximately 100 grams of soil were collected per field.

Method two involved the use of a square of screening wire with mesh size of 1/3 mm. The screen was 75 mm square. The screen was placed over the soil at the edge of the trees' outermost branches and in an area not likely to have been irrigated. The screen was placed under the edge of 20 trees in the field and dust was extracted through the mesh with a portable 12 volt powered vacuum cleaner by covering the screen area twice at each locale. The dust was vacuumed up into disposable bags which were placed in glass jars to be taken to the laboratory. About 30 grams were collected by this method for each field sampled.

Pesticide residues in the soil are a potential hazard for field workers. During harvest, activity in the orchard created by trucks, tractors, workers, and ladders stirs up dust which may settle on leaves, be inhaled or settle on a worker's skin and clothes. Many pesticides, especially parathion and paraoxon, readily enter the body through the skin. During rest periods, workers may remain in the grove and sit on the soil which has been loosened. Dust may collect in the worker's clothes and shoes. If a high level of parathion and particularly paraoxon residue is contained in the dust, skin contact with the dust may present a significant worker safety hazard.

Residue levels and degradation rates are highly variable in the soil due to varying types of soil. Irrigation practices also affect degradation. Drip irrigation leaves most of the orchard dry the majority of the time; this allows residues to remain longer. Furrow irrigation may also leave much of the soil surface dry. Only flood irrigation and sprinkler irrigation, providing the equivalent of more than one inch of rainfall at one time causes rapid degradation of organophosphate pesticides. Nearly all the fields studied were irrigated by furrow irrigation.

The two methods of soil sampling were used for the purpose of comparison of results of analysis. (see Table 5).

When sampling was done with a vacuum, residues of parathion and paraoxon detected were approximately five times greater than when samples are obtained by scraping. This is presumably because the vacuum is more precise in removing a thin and even layer from the top of the soil, where the pesticide residues are more concentrated. This layer is the one to which the worker is most likely exposed.

Overall, these groves had surprisingly high levels of parathion and paraoxon on the soil surface, some with more than 2,128 ppm of parathion equivalents as long as 50 days after application. Scraper sampling of the soil in the grove where the workers became poisoned revealed a level of up to 313 parathion equivalents; this might have been as high as 1,500 ppm had it been sampled by the vacuuming technique.

CONCLUSIONS

High levels of residues of ethyl parathion and its metabolite paraoxon that are considered to be quite hazardous to citrus pickers can occur during the summer months for up to at least 50 days after application in the areas of California where there is little or no rainfall and the weather is hot and sunny.

Residues of parathion are the highest the day of application and the build-up of the more toxic metabolite paraoxon begins several days later. These values are highest on leaves when a pesticide is applied in a small amount of water and applied with "speed-spray" type of equipment. With types of irrigation that allow the foliage and substantial areas of soil to remain dry, the levels of toxic residue persist on foliage and in the soil for a number of weeks. In the past, it had generally been considered safe to enter any treated groves to pick at least by 45 days after application of parathion. Considering the levels of parathion and paraoxon sometimes found, it is doubtful if it is safe to enter some treated grove prior to 60 days after application during hot weather. This is particularly the case in groves where the parathion has been applied as a concentrate in small amounts of water resulting in high foliage residues. On the other hand, very high soil residues appear to be related to applications using approximately 1,000 gallons of water per acre in fields with types of irrigation that leave sizable areas of soil dry.

RECOMMENDATION

For parathion residues which will be exposed to hot dry weather in citrus groves, a 60-day safety interval should be imposed. During the cool months of the year, a 30-day interval should be adequate.

Table 1

Application Information of "99 Row Valencia Block"
Where Workers were Poisoned

Date Parathion Applied:	June 24, 1977
Rate:	20 lbs/acre 25 WP
	(5 lbs active ingredient)
Volume:	100 gal/acre
EPA Reg. No.:	5905-255-AA

Table 2

Foliage Residues of Parathion Where Workers Were Poisoned in Tulare County in July 1977. Samples Collected Two Days After Onset of Illness.

Sample Identification	Total Residues		
	Parathion	Paraoxon	Parathion Equivalents
A	3.8	1.0	58.8
B	10.1	2.6	153.1
C	7.0	2.9	162.4

Sample Number	Surface Residues			Total Residues		
	Parathion	Paraoxon	Parathion Equivs.	Parathion	Paraoxon	Parathion Equivs.
1	trace	4.3	236.5	10.7	3.6	208.7
2	trace	2.3	126.5	12.2	3.7	215.7
10	trace	2.1	115.5	7.2	2.6	150.2
20	trace	2.2	121.0	5.4	2.1	120.9

Table 3

Foliage Residues of Parathion in "99 Row Valencia Block" Where Workers Were Poisoned. Samples Collected Seven Days After Last Day of Exposure Before Onset of Illness.

Sample Number	Surface Residues			Total Residues		
	Parathion	Paraoxon	Parathion Equivs.	Parathion	Paraoxon	Parathion Equivs.
2	0.2	0.6	33.2	5.3	2.0	115.3
1	0.3	0.9	49.8	6.1	2.5	143.6
10	0.3	0.7	38.8	7.6	2.4	139.6
20	0.4	0.7	38.9	6.5	1.6	94.5

Table 4

Parathion Residues in and on the Surface of Oranges Being Picked in "99 Row Valencia Block" Where Pickers were Poisoned in July 1977.

	Parathion	Paraoxon	Parathion Equivalents
Surface of Orange Peel	8.1 ppm	1.5 ppm	86.6
Total Orange	0.5	0.1	6.0

Table 5

Soil Residues of Parathion "99 Row Valencia Block" Where Farm Workers Were Poisoned in July 1977. Samples Were Collected by Scraper Technique Five Days After the Poisoning Incident.

Sample Identification	Total Residues		
	Parathion	Paraoxon	Parathion Equivalents
A	1.5	0.7	40.0
B	5.1	4.8	269.1
C	22.4	5.3	313.9

Table 6

Comparison of Residues on Orange Leaves Sampled by Two Methods.

Surface Residues			
Parathion		Paraoxon	
Punch	Whole Leaf	Punch	Whole Leaf
0.17	-	0.26	-
-	-	0.09	0.40
<0.1	-	0.30	0.27
$\overline{X}$ = 0.01	$\overline{X}$ = 0.00	$\overline{X}$ = 0.22	$\overline{X}$ = 0.22

Total Residues			
Parathion		Paraoxon	
Punch	Whole Leaf	Punch	Whole Leaf
14.4	10.6	3.0	3.4
7.2	12.2	1.5	3.6
14.4	8.8	3.3	3.3
$\overline{X}$ = 12.0	$\overline{X}$ = 10.5	$\overline{X}$ = 2.6	$\overline{X}$ = 3.4

Table 6

Results

Study of Parathion and Paraoxon Residues on Citrus Foliage and Soil in Fresno and Tulare Counties During Summer of 1977

Field Number	Days After Application	Leaf Residue						Soil Residue					
		Surface Residue			Total Residue			Scraper			Vacuum		
		Parathion	Paraoxon	Parathion* Equivalents	Parathion	Paraoxon	Parathion Equivalents	Parathion	Paraoxon	Equivalents	Parathion	Paraoxon	Equivalents
01	23	<0.1	<0.1	<0.1	2.1	<0.1	2.1	17.8	4.2	248.8	-**	-	-
	30	<0.1	<0.1	<0.1	0.8	<0.1	0.8	2.3	2.3	128.8	8.0	6.2	349.0
	39	-	-	-	-	-	-	2.2	1.7	95.7	6.7	2.9	166.2
02	28	<0.1	<0.1	<0.1	13.3	1.3	84.8	1.2	1.0	56.2	-	-	-
	35	<0.1	<0.1	<0.1	7.6	1.1	68.1	1.4	4.1	226.9	-	-	-
	44	-	-	-	-	-	-	0.6	0.8	44.6	1.6	2.4	133.6
03	34	<0.1	<0.1	<0.1	14.2	0.4	36.2	-	-	-	-	-	-
	41	.02	<0.1	<0.1	4.4	0.3	20.9	2.0	2.3	128.5	-	-	-
04	22	<0.1	<0.1	<0.1	3.7	1.3	75.2	2.4	2.4	134.4	4.2	12.3	680.7
	28	<0.1	<0.1	<0.1	1.6	<0.1	1.6	2.1	0.5	29.6	-	-	-
05	34	0.1	<0.1	<0.1	16.3	2.4	148.3	4.3	3.8	213.3	-	-	-
	40	<0.1	<0.1	<0.1	21.1	1.6	109.1	2.7	3.0	167.7	-	-	-
	48	-	-	-	-	-	-	2.6	4.0	222.6	7.3	23.6	1305.3
06	30	0.2	<0.1	0.2	0.8	0.3	17.3	2.4	2.5	139.9	-	-	-
	37	<0.1	<0.1	<0.1	1.8	0.6	34.8	1.7	1.8	100.7	-	-	-
	44	-	-	-	-	-	-	1.3	1.6	89.3	1.8	9.8	540.8
07	29	0.1	0.1	5.6	0.6	0.5	28.1	16.4	3.9	230.9	-	-	-
	36	<0.1	<0.1	<0.1	0.2	<0.1	0.2	10.7	2.6	153.7	-	-	-
	42	-	-	-	-	-	-	1.0	0.2	12.0	0.9	0.5	28.4
08	21	0.1	0.1	5.6	7.2	2.2	128.2	2.8	1.3	74.3	15.1	8.4	477.1
	27	<0.1	0.2	11.0	6.9	0.9	56.4	1.7	0.4	23.7	6.2	1.9	110.7
09	17	<0.05	<0.05	<0.05	2.9	2.3	129.4	4.7	5.6	312.7	-	-	-
	23	<0.1	0.2	11.0	3.3	0.7	41.8	0.5	0.7	39.0	-	-	-
	31	-	-	-	1.4	0.5	28.9	-	-	-	-	-	-
10	18	0.1	0.1	5.6	4.3	2.0	114.3	1.6	1.4	78.6	-	-	-
	24	0.1	0.1	5.6	<0.1	<0.1	<0.1	2.1	6.0	332.1	62.1	<0.1	62.1
	32	-	-	-	2.7	0.8	46.7	-	-	-	-	-	-
11	52	0.04	<0.1	0.04	2.2	0.4	24.2	0.8	0.8	44.8	-	-	-
	58	<0.01	<0.01	<0.01	1.7	0.3	18.2	-	-	-	1.5	1.1	62.0
	63	-	-	-	-	-	-	0.3	0.2	11.3	1.5	0.9	5.1
12	43	<0.05	<0.05	<0.05	3.7	0.8	47.7	1.1	1.0	56.1	-	-	-
	49	<0.01	<0.01	<0.01	3.2	0.7	41.7	-	-	-	5.5	4.1	231
	57	-	-	-	-	-	-	0.9	0.7	39.4	3.3	2.3	129.8
13	45	<0.01	<0.01	<0.01	2.8	0.7	41.3	2.9	3.9	217.4	-	-	-
	51	<0.05	<0.05	<0.05	1.2	0.2	12.2	-	-	-	31.3	26.3	1477.8
	59	-	-	-	-	-	-	4.2	8.1	449.7	6.2	19.0	1051.2
14	36	0.04	0.04	2.2	2.6	0.7	42.2	10.9	13.1	731.4	-	-	-
	42	<0.1	<0.1	<0.1	3.7	0.4	25.7	1.6	3.0	166.6	-	-	-
	50	-	-	-	-	-	-	20.3	15.6	878.3	16.4	38.4	2128.4
15	47	0.01	0.01	5.6	7.4	0.9	56.9	9.1	8.1	454.6	-	-	-
	53	<0.1	<0.1	<0.1	4.8	0.4	26.8	5.8	5.7	319.3	-	-	-
	61	-	-	-	-	-	-	2.5	4.6	255.5	4.0	11.5	636.5
16	46	0.05	0.03	1.7	1.8	0.3	18.3	3.5	3.7	207.0	-	-	-
	52	<0.1	<0.1	<0.1	1.7	0.3	18.2	1.6	1.6	89.6	-	-	-
17	11	0.2	0.1	5.7	1.2	0.6	34.2	48.1	4.7	306.6	-	-	-
	18	<0.1	<0.1	<0.1	0.7	0.3	17.2	31.2	7.4	438.2	-	-	-
	24	-	-	-	-	-	-	12.4	4.2	243.4	34.6	32.5	1822.1
18	44	0.2	0.3	16.7	14.4	3.0	179.4	3.4	6.0	333.4	2.9	10.8	596.9
	44	<0.1	0.1	5.5	7.2	1.5	89.7	1.3	3.0	166.3	3.2	14.5	800.7
	44	<0.1	0.3	16.5	14.4	3.3	195.9	1.9	2.0	111.9	5.9	25.2	1391.9

* Parathion residue in ppm + (paraoxon residue in ppm x 55)
** No sample collected

Table 7

Weather Data for Northern Tulare County and Southern Fresno County*
During May, June, July, and August of 1977

Tulare Co.	Temperature Maximum	Temperature Minimum	Precipitation (Inches)
May 15	76	49	
16	75	47	
17	67	44	
18	71	44	
19	74	49	
20	76	44	
21	85	57	
22	88	55	
23	80	51	0.03
24	71	51	
25	76	51	
26	78	51	
27	80	54	
28	80	50	
29	82	53	
30	87	53	
31	93	59	
Average	78.8	50.7	Total 0.03
June 1	100	63	
2	96	57	
3	91	57	
4	92	59	
5	94	58	
6	95	69	
7	101	71	
8	107	71	
9	94	68	0.05
10	82	58	
11	75	54	
12	84	55	
13	87	42	
14	85	55	
15	84	54	
16	91	59	
17	90	57	
18	89	57	
19	88	58	
20	88	60	
21	89	59	
22	96	71	
23	104	68	
24	103	69	
25	104	71	
26	107	70	
27	103	68	
28	106	67	
29	99	76	
30	97	69	
Average	94.0	62.3	Total 0.05
July 1	101	70	
2	99	66	
3	93	67	
4	94	61	
5	88	56	
6	89	60	
7	93	60	
8	98	62	

Tulare Co.	Temperature Maximum	Temperature Minimum	Precipitation (Inches)
July 9	99	61	
10	95	60	
11	95	62	
12	99	64	
13	98	61	
14	96	62	
15	98	65	
16	101	67	
17	96	71	
18	103	68	
19	101	62	
20	96	65	
21	96	65	
22	98	62	
23	97	62	
24	98	63	
25	96	59	
26	93	58	
27	96	60	
28	97	62	
29	98	61	
30	99	69	
31	103	70	
Average	96.9	63.3	Total 0.00
Aug 1	103	71	
2	102	74	
3	104	69	
4	101	68	
5	97	64	
6	97	61	
7	93	56	
8	87	56	
9	90	61	
10	91	61	
11	95	62	
12	98	66	
13	98	65	
14	96	60	
15	94	61	
16	97	67	
17	89	74	
18	79	69	0.13
19	92	67	
20	95	65	
21	95	62	
22	93	61	
23	100	61	
24	100	62	
25	90	62	
26	88	62	
27	85	58	
28	88	57	
29	93	66	
30	96	65	
31	96	63	
Average	94.3	63.8	Total 0.13

References

Gunther, F. A. et. al.; "The Citrus Reentry Problem: Research on its causes and effects, and approaches to its minimization." reprint from RESIDUE REVIEWS, Volume 67 (1977).

Nabb, D. P., 35 et. al.; "Rate of Skin Absorption of Parathion and Paraoxon." Arch. Environ. Health 12, 501 (1966).

APPENDIX

ANALYTICAL METHODS (EXTRACTION)

The procedure used for the extraction of dislodgeable, penetrated, and total residues from leaf punches was originally published by Gunther in "The Bulletin of Environmental Contamination and Toxicology", 9, 243-249, 1973. It has been documented several times in detail, with modifications that were made to accommodate the various pesticides and their metabolites, that the Worker Health and Safety Unit has been concerned with.

The sample container and leaf punches are weighed and the gross weight recorded.

Total Residues

1. The leaf punches are transferred to a blending jar. The empty sample container is again weighed and the net weight of the punches recorded.

2. Approximately 50 gms of sodium sulfate and 100 mls of acetone or ethyl acetate are added.

3. The sample is blended at high speed for 3 minutes, keeping the blender cup cool by immersing it in a container of cool water. The blender cup is removed and the sample allowed to settle.

4. An aliquot is decanted into a teflon-capped bottle and stored in the freezer prior to clean up and analysis.

Dislodgeable Residues

1. Fifty mls of water and approximately 4 drops of Sur-Ten solution (1:50) are added to the sample containers. The containers are capped and placed in a multi-purpose rotator and rotated at 30 cycles/min. for 60 minutes. The aqueous solution is decanted through a glass wool plug into a 500 ml separatory funnel.

2. The punches are rotated a second time, using 50 mls of water and 4 drops of Sur-Ten solution, for 30 minutes. This is added to the first extraction.

3. The sample is then hand-shaken for approximately 10 secs with 30 mls of water. The container is drained into the separatory funnel with the first two extractions.

ANALYTICAL METHODS (CHROMATOGRAPHY)

GLC Conditions:

Varian 2700, FPD detector, std. flows, 6' x 2 mm I.D. of 3% OV-101 at 185° C, 40 psi head pressure, 30 cc N_2 as a carrier.

Varian 2100, FPD detector, std. flows, 5.25' x 2 mm I.D. of 3% OV-101 (carbowax vapor deposition treated) at 185° C, 26% flow.